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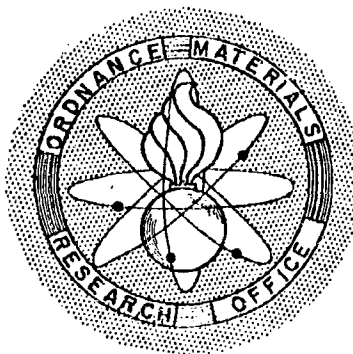
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EXCHANGE POLARIZATION AND THE MAGNETIC
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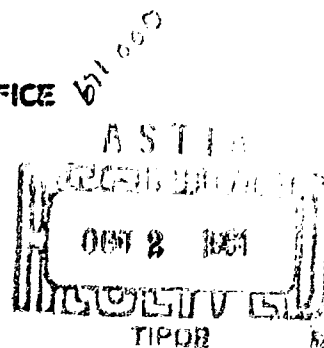
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R. E. WATSON
A. J. FREEMAN

FEBRUARY 1961



MATERIALS RESEARCH LABORATORY
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WATERTOWN 72, MASSACHUSETTS



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EXCHANGE POLARIZATION AND THE MAGNETIC INTERACTIONS
OF RARE EARTH IONS[†]

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Abstract

Results are reported of a study of the contribution of spin or exchange polarization to the magnetic interaction of a rare earth ion with its neighbors and with its own conduction electrons. The rare earth ions carry a "paired" electron spin density which is negative in their outer reaches and these ions may even appear to their neighbors as having negative spins (i.e. antiparallel to the 4f spin direction). Some experimental results are discussed on this basis.

*Guests of the Solid State and Molecular Theory Group, M.I.T.

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We are reporting results of a study of the contribution of spin or exchange polarization⁽¹⁾ to the magnetic interaction of a rare earth ion with its neighbors and with its own conduction electrons. This investigation was carried out by means of conventional analytic Hartree-Fock calculations⁽²⁾ for the Gd^{+3} and Gd^{+} ions and a spin polarized H-F calculation⁽²⁾ for the Gd^{+3} ion. While the conventional H-F results are of interest in themselves, since they represent the first time such information has been available for the rare earths, we shall only discuss a result of the spin polarized calculation which may have important consequences for the magnetic behavior of these elements. Our results suggest that the rare earth ions carry a "paired" electron spin density which is negative in their outer reaches. Since the unfilled 4f shell electrons are imbedded in the interior regions of the ions, this outer spin distribution can play an important (and perhaps even dominant) role in the magnetic interactions of rare earth ions. In fact, as will be shown, these ions may even appear to their neighbors as having negative spins (i.e. antiparallel to the 4f spin direction) and some experimental results are discussed on this basis.

The contribution of "paired" electrons to the magnetic properties of solids has been the object of recent studies^(2,3) which have utilized the spin polarized Hartree-Fock method. Two effects have been studied. The first of these is the contribution of the core s electrons, via the Fermi contact term, to the effective magnetic field at a nucleus in a ferromagnet.⁽³⁾ This contribution appears to be the dominant source of the recently observed negative effective⁽⁴⁾ fields in ferromagnets. Secondly, computations^(2,5) for the contribution of the "paired" electron spin density⁽⁶⁾ to an ion's neutron form factor suggest that the contribution is observable, a suggestion which has been borne out by a recent neutron diffraction investigation⁽⁷⁾ for NiO. This letter discusses a third aspect of such spin polarization in solids, namely its contribution to an ion's magnetic interaction with neighboring ions and conduction electrons. The Gd^{+3} ion's unpaired 4f electrons, which are well in its interior, supply an extreme test of the effect. In what follows we presume that the free ion results are a reasonable description of the Gd "core" electrons in a solid, a not uncommon assumption. The neglect of important relativistic effects, limitations in the spin polarized formalism⁽²⁾ and limitations in computational accuracy for an ion of so high an atomic number make it advisable to view the results which follow for qualitative rather than detailed quantitative behavior.

Figure 1 shows the computed "core" electron spin density ($\rho_{\uparrow} - \rho_{\downarrow}$) for all the electrons other than the 4f shell and, for comparison, the 4f density as well. (Note the change of scales at $r=3.0$ au to a common scale for both $\rho_{\uparrow} - \rho_{\downarrow}$ and the 4f density.) The two negative regions indicate densities associated with a spin antiparallel to the net spin of the ion. The region near the nucleus produces the negative effective fields of the type already discussed⁽³⁾ for iron. The outer region⁽⁸⁾ is important for interactions with neighboring atoms and two examples are discussed below.

NMR studies⁽⁹⁾ in magnetic crystals have revealed large internal magnetic fields at the nuclei of normally diamagnetic atoms like F^- . The hyperfine interactions between the fluorine nucleus and the 3d magnetic electrons of the transition metal ion have been interpreted as arising from unpaired spins in the fluoride ion orbitals. This unpairing is thought to arise in either of two distinct ways: (1) because of an admixture of covalent bonding into the purely ionic configuration⁽¹⁰⁾ or (2) by the unpairing action of the Pauli principle ("Pauli distortion")⁽¹¹⁾ which affects those fluorine orbitals which have the same spin as the cation 3d orbital differently from those orbitals which have opposite spin. In either method the unpaired 2s electrons produce an isotropic hyperfine interaction whereas the 2p electrons produce an anisotropic interaction, the degree of unpairing being determined by the squares of the overlap integrals, (S^2) , between the free F^- orbitals and the 3d electrons on the cation. Let us consider the application of this type of analysis to a rare earth salt such as GdF_3 in order to explore the consequences of the negative spin density in the outer region of the Gd^{+3} ion. Since the "paired" orbitals (5s and 5p) have different radial distributions they will overlap the fluoride orbitals differently and it is this difference in their interactions which gives rise to a hyperfine interaction with the fluorine nucleus. Denoting the Gd^{+3} 4f shell spin as up (\uparrow) then the extent of the interaction is measured by $S_i^2(\uparrow) - S_i^2(\downarrow)$ where i denotes some pairs of electrons. In Table I we list the square of the overlap integrals between the Gd^{+3} 4f(\uparrow), 5s (\uparrow and \downarrow), and 5p (\uparrow and \downarrow) and the F^- Hartree-Fock⁽¹²⁾ 2s orbital at the observed⁽¹³⁾ nearest neighbor distance of 4.4 au. (For lack of space the anisotropic (2p) interaction will not be discussed here.) We see that the sum of S_i^2 is greater than the sum of S_i^2 and that $\sum S_i^2 - \sum S_i^2$ gives an effect which is ten times as large and opposite in sign to that obtained by considering the 4f overlap alone. In other words, in the context of either the Pauli distortion or covalency mechanisms (2 and 1 above), our spin polarized functions predict that a Gd^{+3} ion, as seen by a nearest neighbor F^- ion, appears (in its interactions) to have a spin which is anti-parallel to the actual Gd^{+3} spin.⁽¹⁴⁾

Jaccarino et al.⁽¹⁵⁾ have reported the NMR of Al^{27} in the rare-earth intermetallic compounds and have interpreted the observed negative Knight shift as arising via the Ruderman-Kittel-Kasuya-Yosida⁽¹⁶⁾ mechanism from a negative exchange interaction between the localized 4f electrons and conduction electrons. We have calculated overlap integrals and simple electrostatic exchange integrals $\langle \frac{1}{r_{12}} \rangle$ (which are important for direct magnetic interactions) between the Gd^{+3} spin polarized functions and Hartree-Fock Al wave functions⁽¹⁷⁾ at the observed $GdAl_2$ internuclear distance of 6.2 au. The outer region of negative spins again dominates over the 4f interaction for both the S^2 's and the $\langle \frac{1}{r_{12}} \rangle$ integrals, i.e., the Gd^{+3} ion again behaves as if it had a negative spin. In fact these outer "core" electrons account for about one-tenth of the observed Knight shift⁽¹⁶⁾ and is of the correct (i.e. negative) sign. In the metal the conduction electrons (which have not been included in our calculations) would also have a "paired" negative spin density in their outer regions and since their overlap with the Al functions would

be greater than that of the "core" functions their contribution to the hyperfine field at the Al nucleus would also be correspondingly greater. It is therefore possible that the observed negative Knight shift could be interpreted as arising from exchange polarization without invoking a negative exchange interaction between the localized 4f electrons and the conduction electrons.

We also studied the exchange interaction between a spin polarized Gd^{+3} ion and conduction electrons in the metal. The "conduction" electrons were assumed to be 6s electrons (which we obtained from a conventional and more accurate H-F calculation for the free Gd^{+3} ion) and exchange integrals were calculated between this 6s electron and the spin polarized Gd^{+3} orbitals. In this case the 4f exchange interaction (i.e. between the 4f \uparrow and 6s \uparrow electrons) was found to dominate over the net exchange interaction (i.e. the difference in exchange between the "core" \uparrow and \downarrow spins with the 6s electrons) which was negative and about one-fifth that of the 4f electrons, in agreement with Hund's rule for localized interactions.

These investigations and related ones on the magnetic interactions of rare earth ions will be discussed at length in a forthcoming publication.

We are grateful for the assistance of R. K. Nesbet, stimulating conversations with A. M. Clogston, V. Jaccarino, and M. Peter, and the help of A. Switendick with his computer programs.

TABLE I: The square of the overlap integrals, S^2 , between the Gd^{+3} outer orbitals and the F^- 2s orbital at the nearest neighbor distance of 4.4 au and the net contribution to the internal field at the F^- nucleus ($\Sigma S_{\uparrow}^2 = \Sigma S_{\downarrow}^2$).

$4f \uparrow - 2s$	$.012 \times 10^{-2}$		
$5p \uparrow - 2s$	$.365 \times 10^{-2}$	$5p \downarrow - 2s$	$.483 \times 10^{-2}$
$5s \uparrow - 2s$	$.085 \times 10^{-2}$	$5s \downarrow - 2s$	$.107 \times 10^{-2}$
$\Sigma S_{\uparrow}^2 =$	$.462 \times 10^{-2}$	$\Sigma S_{\downarrow}^2 =$	$.590 \times 10^{-2}$

Net effect = $\Sigma S_{\uparrow}^2 - \Sigma S_{\downarrow}^2 = -.128 \times 10^{-2}$ (equivalent to - 7200 gauss at the F^- nucleus). Contribution from the 4f shell alone = $+.012 \times 10^{-2}$ (equivalent to + 700 gauss).

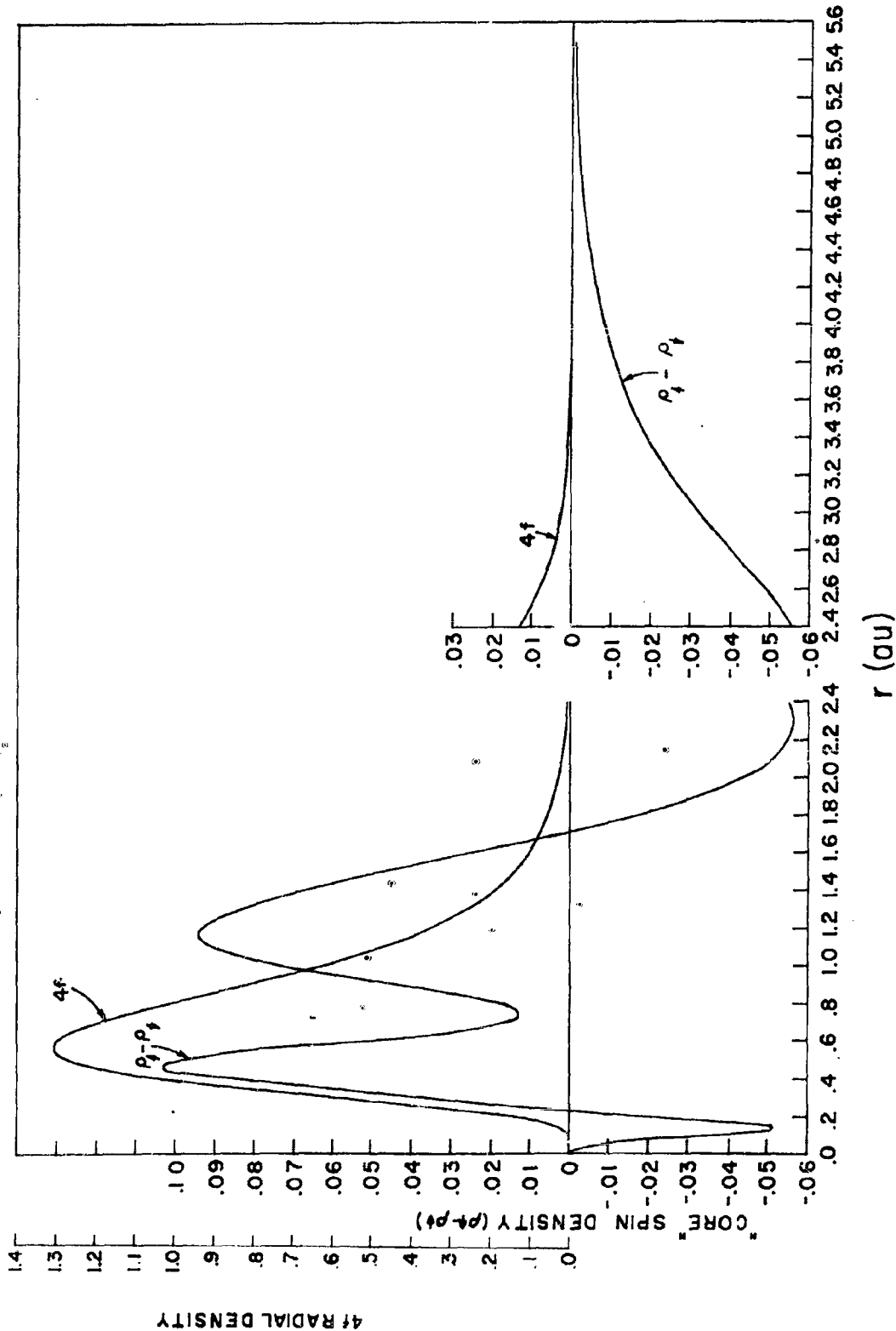


FIG. 1 THE COMPUTED "CORE" ELECTRON SPIN DENSITY ($\rho_{\uparrow} - \rho_{\downarrow}$) FOR ALL THE ELECTRONS OTHER THAN THE 4f SHELL AND, FOR COMPARISON, THE 4f DENSITY AS WELL. NOTE THE CHANGE OF SCALES AT $r = 3.0$ au TO A COMMON SCALE FOR BOTH ($\rho_{\uparrow} - \rho_{\downarrow}$) AND THE 4f SPIN DENSITY.

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